

Mixed Allyl Ethers of Starch¹

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A number of mixed ethers of starch containing both allyl and saturated alkyl groups have been prepared. These ethers do not contain free hydroxyl groups, and some of them are soluble in aliphatic hydrocarbons, in which the previously described allyl starch is insoluble. Solubility relations and specific rotations of the mixed ethers are given.

ALLYL ether of starch containing about two allyl groups per glucose unit was described previously (10). Further allylation is extremely slow, and the product obtained is tacky. Owing to difficulty in handling and purification, its properties are difficult to study. However, since there might be certain advantages in an ether containing no hydroxyl groups, it seemed advisable to introduce other ether groups into the partially substituted allyl starch. In actual practice the reverse procedure was used. The starch was etherified to various degrees of substitution with an alkyl group and then allylated to complete substitution. In this manner the danger of formation of addition products or polymerization of the allyl starch was eliminated. Besides, owing to the greater reactivity of allyl halides as compared with saturated alkyl halides, it appeared probable that it would be easier to allylate partially etherified starch than to etherify allyl starch further with a saturated halide group.

Several alkyl derivatives of starch have been reported in the literature. Methyl starch was prepared by the direct action of methyl sulfate on starch (4) and by simultaneous hydrolysis and methylation of starch acetate (3). The ethyl ether may be obtained by the method of Lilienfeld (7). Highly degraded propyl and butyl ethers of starch were reported by Degering and Rankin (6). The higher alkyl derivatives apparently have not been previously prepared.

An attempt was made to find a single method for alkyl ethers of starch which would be applicable to all the compounds to be prepared. The method of Haworth, Hirst, and Webb for methylation of starch was satisfactory for introducing ethyl groups but did not give good products with butyl or amyl groups. Both the direct etherification method, as employed by Irvine and Macdonald, and a method similar to the one used for the preparation of allyl starch gave a low substitution with higher alkyl derivatives. The substitution remained low even after pretreatment of starch with liquid ammonia or after treatment with sodium amide in liquid ammonia and subsequent etherification with alkyl halide (1, 2, 9, 11). On the other hand, Lilienfeld's method (7), in which both the alkali and the etherifying agent are added in several steps, produced compounds of considerably higher substitution. Thus by the action of butyl bromide on starch (using the same molar ratio of all constituents), a product containing 2.4 butyl groups per glucose unit was obtained after 16 hours; a one-step method similar to that used for the preparation of allyl starch gave a product with 0.4 group per glucose unit. Similarly, with butyl iodide the first method produced a compound with 1.3 groups in 2 hours, whereas the second gave a product with only 0.5 group in 4 hours. Lilienfeld's method consists of three steps. In the first, the starch is prepared for etherification, and part of the alkali is added. In the second, more alkali and a portion of the etherifying agent are added. In the last step the alkali concentration is increased to 50%, and the rest of the etherifying agent is added. The method was modified here with regard to quantity of alkali, temperature, and reaction time. Under the same conditions the extent of substitution was controlled by the amount of etherifying agent used in steps 2 and 3. Table I shows the results and also indicates the solubilities of various preparations in a number of solvents. The yields rose with increase in substitution, which was to be expected, although it was partly due to the greater ease in isolating the more highly substituted ethers.

¹ This is the fourth paper in a series from this laboratory on Allyl Ethers of Carbohydrates.

TABLE I. PREPARATION AND PROPERTIES OF SIMPLE ETHERS

TABLE I. PREPARATION AND PROPERTIES					Solubility ^a in:								
Etherifying Agent	Grams Used for 20 G. Starch		Ether Groups per Glucose Unit	Yield, Grams	Cold water	Hot water	Pyridine	Ethylene chlorohydrin	Chloroform	Alcohol	Benzene	Skellysolve B	Acetone
	Step 2	Step 3											
Ethyl sulfate	60	None	0.5	13	ss	i	i	i	i	i	i	i	i
	40	100	1.1	18	s	i	s	ss	i	i	i	i	ss
	40	240	1.6	19	ss	i	s	s	ss	i	i	i	s
	60	360	2.1	20	i	i	s	s	s	s	ss	i	s
	80	480	2.8	24	i	i	s	s	s	s	s	i	s
Propyl bromide	22.7	11.4	0.7	9	s	i	s	s	i	i	i	i	i
	22.7	22.8	1.3	11	ss	i	s	s	s	s	ss	i	ss
	45.5	45.5	1.7	13	i	i	s	s	s	s	s	i	s
	91.0	91.0	2.5	28	i	i	s	s	s	s	s	i	s
Butyl iodide	15	None	0.5	18	s	ss	i	i	i	i	i	i	i
	10	10	1.1	18	ss	i	s	s	ss	s	i	i	ss
	12.5	12.5	1.5	19	i	i	s	s	s	s	ss	s	s
	25	25	2.1	29	i	i	s	s	s	i	s	s	s
	50	50	2.6	30	i	i	s	s	s	i	s	s	s
Amyl bromide	7.0	None	0.4	14	s	ss	i	i	i	i	i	i	i
	7.0	7.0	1.3	17	i	i	s	s	s	ss	ss	i	i
	14.0	7.0	1.9	17	i	i	s	s	s	i	s	ss	i
	27.8	27.8	2.6	34	i	i	s	s	s	i	s	s	i
	55.6	55.6	2.8	36	i	i	s	s	s	i	s	s	i
Hexyl iodide	20	20	0.6	12	ss	i	s	ss	ss	ss	i	i	i
	40	40	1.0	14	i	i	s	s	s	ss	ss	i	i
	100	100	1.6	29	i	i	s	s	s	i	s	s	i
	100	100 ^b	2.2	30	i	i	s	s	s	i	s	s	i
Heptyl iodide	10.5	None	0.5	13	s	i	ss	ss	ss	ss	i	i	i
	20.9	None	0.8	23	i	i	s	s	ss	ss	i	i	i
	31.4	None	0.9	27	i	i	s	s	s	ss	i	i	i
	20.9	20.9	1.7	33	i	i	s	s	s	i	s	s	i
	41.8	41.8	2.6	39	i	i	s	s	s	i	s	s	i
Lauryl iodide	37.4	37.4 ^b	0.5	13	i	i	s	ss	ss	i	i	i	i
	54.8	54.8 ^b	0.7	14	i	i	s	s	ss	i	i	i	i
	109.6	109.6 ^b	0.9	17	i	i	s	s	s	i	s	s	i
	164.6	164.6 ^b	1.1	18	i	i	s	s	s	i	s	s	i

^a s = soluble; ss = slightly soluble; i = insoluble.^b Heated in final stage for 16 hours instead of usual 3 hours.

The alkyl ethers thus obtained were dissolved or suspended in methyl ethyl ketone and etherified with allyl bromide in the presence of alkali. Table II describes the composition and properties of mixed ethers. The specific rotation of all the ethers except ethyl-allyl decreased as the proportion of allyl to the other groups decreased. The solubility of mixed allyl ethers of starch depended on the chain length and relative amount of the saturated ether group. With increase of both factors, the solubility in Skellysolve B and *n*-heptane increased, and the solubility in alcohol decreased. Thus, neither ethyl-allyl nor propyl-allyl starches were soluble in aliphatic hydrocarbons. The introduction of 1.5 butyl, 1.3 amyl, 1.0 hexyl, and 0.9 heptyl or lauryl group made the starch ethers soluble in *n*-heptane and Skellysolve B and insoluble in alcohol. The yields of mixed allyl ethers were all in the neighborhood of 90% of theory.

Polymerization of mixed ethers proceeded essentially in the same manner as that of straight allyl ethers. Thin films deposited from an organic solvent gradually insolubilized on heating in the presence of air or oxygen, if the mixed ether contained about 1.5 or more allyl groups. Paint driers—for example, cobalt naphthenate—accelerated polymerization. The increase in the chain length of the saturated group appeared to retard polymerization.

I. PREPARATION OF SIMPLE SATURATED ETHERS

As an example of the preparation of simple saturated starch ethers, that of butyl starch will be described in detail. The reaction was carried out in a three-neck one-liter flask fitted with a mechanical stirrer and reflux condenser. The flask was heated in a temperature-controlled oil bath at various temperatures:

1. To 20 grams of dry potato starch slurried in 300 grams of water for 30 minutes at room temperature, 100 grams of 40% sodium hydroxide were added, and the mixture was heated for 30 minutes at 65° C. with rapid stirring (Hershberg stirrer). During this operation the starch gel was broken down to a thin clear paste.

TABLE II. PROPERTIES OF MIXED ETHERS

Compn., Groups per Glucose Unit		Yield, Grams per 10 G. of Simple Ether	Solubility ^a	[α] _D ²⁵ in Chloroform
Allyl	Other			
2.6	0	..	A	142.8
2.4	0.5 ethyl	15	A	150.1
1.8	1.1 ethyl	14	A	152.3
1.4	1.6 ethyl	12	A	154.2
1.0	2.1 ethyl	11	A	157.4
0	2.8 ethyl	162.2
2.3	0.7 propyl	14	A	131.2
1.7	1.3 propyl	13	A	125.2
1.2	1.7 propyl	12	A	124.1
0.6	2.5 propyl	11	A	123.4
0	2.5 propyl	123.1
2.5	0.5 butyl	15	A	133.9
1.9	1.1 butyl	13	A	123.8
1.4	1.5 butyl	12	B	130.9
0.9	2.1 butyl	11	B	127.9
0.5	2.6 butyl	10	B	122.9
0	2.6 butyl	119.2
2.5	0.4 amyl	15	A	116.2
1.6	1.3 amyl	12	B	108.2
1.2	1.9 amyl	11	B	107.5
0.6	2.6 amyl	11	B	105.7
0	2.8 amyl	102.2
2.4	0.6 hexyl	15	A	134.3
2.1	1.0 hexyl	13	B	127.6
1.6	1.6 hexyl	12	B	122.2
0.8	2.2 hexyl	11	B	117.2
2.4	0.5 heptyl	14	A	127.5
2.3	0.8 heptyl	14	A	120.2
2.2	0.9 heptyl	14	B	118.5
1.4	1.7 heptyl	12	B	107.0
0.4	2.6 heptyl	10	B	100.6
0	2.6 heptyl	96.4
2.4	0.5 lauryl	14	A	129.2
2.3	0.7 lauryl	13	A	126.1
2.0	0.9 lauryl	13	B	121.6
1.9	1.1 lauryl	12	B	107.0

^a A = soluble in acetone, benzene, toluene, alcohol, chloroform; insoluble in Skellysolve B and *n*-heptane. B = soluble in acetone, benzene, toluene, chloroform, Skellysolve B, *n*-heptane; insoluble in alcohol.

2. To the clear paste 115 grams of solid sodium hydroxide and 50 grams of butyl iodide were added, and the mixture was heated with continuous stirring for one hour at 95° C.

3. Additional amounts of solid sodium hydroxide (240 grams) and butyl iodide (50 grams) were added, and the temperature was raised to 105° C. for 2 hours, then to 118° for 3 hours.

The reaction mixture was then cooled and neutralized with 50% acetic acid, and the resulting product was filtered and washed with hot water until free of salt. (For products of low substitution the neutralized reaction mixture was heated to 90° C. to precipitate the ether.) The ether was then dried in vacuo for 5 hours at 60°. The yield of white powder was 30 grams, and the substitution was 2.6 butyl groups per glucose unit.

The temperatures given were used in the preparation of all except the ethyl ethers, for which 60° C. was employed in all three steps, and propyl ethers, for which 65° was used in the first step and 78° in the other two. The reaction time was substantially the same for all ethers prepared, with the exceptions indicated in Table I. The drying temperatures (in vacuo) for various ethers were: ethyl, 100° C.; propyl, 90°; butyl, 60°; amyl, 55°; hexyl, 50°; heptyl and lauryl, 40°. All were dried to constant weight.

II. ALLYLATION OF PARTIALLY SUBSTITUTED ETHERS

Ten grams of partially substituted ether were dissolved or suspended in 50 cc. of methyl ethyl ketone in a flask fitted with a reflux condenser and a stirrer. Forty grams of 50% sodium hydroxide and 100 grams of allyl bromide were added, and the mixture was heated for 6 hours at reflux temperature. The solvent and the excess of allyl bromide were then removed by steam distillation, and the gummy product obtained was washed with warm water until free of salt. The mixed ethers were purified by dissolving in acetone and precipitating with water. After several purifications the mixed ethers with short saturated alkyl chains were white powders, whereas those with longer chains had a waxy appearance. All mixed ethers described in Table II were prepared by procedures I and II.

III. DIRECT PREPARATION OF MIXED ALLYL ETHERS

Twenty grams of starch were treated according to procedure I. After the mixture was heated for 3 hours at 118° C., the temperature of the bath was lowered to 80° and 100 grams of allyl bromide were added. The temperature and stirring were maintained for 6 hours. The product was then steam-distilled and purified as described under procedure II.

Thus a butyl ether was prepared by using 12.5 grams of butyl iodide in steps 2 and 3 of procedure I. Then, without isolating the product, 100 grams of allyl bromide were added. The resulting butyl-allyl ether had an allyl content of 18.7% and no free hydroxyl groups. The composition, therefore, as calculated from the formula given later, was 1.4 allyl groups and 1.6 butyl groups per glucose unit. Its specific rotation in chloroform (130.0°) and solubility characteristics agreed closely with those of the almost identical ether described in Table II. Hexyl-allyl ether prepared in a similar manner (100 grams of hexyl iodide in steps 2 and 3, 100 grams of allyl bromide) had an allyl content of 15.2% and no free hydroxyl groups. Its composition was 1.7 hexyl and 1.3 allyl groups. The specific rotation (122.0°) and solubility relationship agreed closely with those of the almost identical ether described in Table II.

ANALYTICAL PROCEDURES. Straight ethyl starch was analyzed by the Zeisel method, and the results were checked by the determination of free hydroxyl groups (8). The results for several ethyl ethers were as follows: Ethyl groups per glucose unit (Zeisel method) were 2.8, 1.7, 1.1; corresponding figures obtained by the free hydroxyl method were 2.8, 1.8, 1.0. The agreement between the two methods is important because the Zeisel method cannot be used for ethers above ethyl, and the value for

substitution is based on the determination of free hydroxyl only. For mixed ethers the number of saturated alkyl groups was determined as described; after allylation the unsaturation was determined by the Wijs method, and from this value the number of allyl groups added was calculated. For determination of unsaturation, the sample was purified by several reprecipitations from acetone solution with water, ground with powdered solid carbon dioxide (to prevent oxidation and facilitate the grinding), and allowed to stand overnight in a vacuum desiccator over phosphorus pentoxide. Samples (0.1 gram) were dissolved in 20 cc. of ethylene chlorohydrin in iodine flasks. To the solution 20 cc. of Wijs solution prepared according to Kemp and Mueller (5) were added, and the flasks were kept in the dark for 4 hours. The mixture was then titrated with 0.1 N sodium thiosulfate.

When mixed allyl ethers are prepared by the direct method (III), the degree of substitution with saturated groups is unknown. In that case only the unsaturation (per cent allyl) and the free hydroxyl can be determined. The substitution of various groups can be determined from the following three equations:

$$P_A = \frac{41N_A 100}{162 - N_S - N_A + SN_S + 41N_A} \quad (1)$$

$$P_H = \frac{17N_H 100}{162 - N_S - N_A + SN_S + 41N_A} \quad (2)$$

$$N_S + N_A[+N_H] = 3 \quad (3)$$

where P_A , P_H = percentages of allyl and hydroxyl as determined by analysis

N_A = number of allyl groups

N_S = number of saturated alkyl groups

N_H = number of hydroxyl groups per glucose unit

S = molecular weight of saturated alkyl radical

Since the mixed ethers described here had no free hydroxyl groups, Equation 2 and the bracketed member of Equation 3 can be eliminated in calculating the number of substituent groups. On solving the two equations for the number of allyl groups, the following is obtained:

$$N_A = \frac{(159 + 3S)P_A}{4100 + P_A(S - 41)}$$

SPECIFIC ROTATION. Mixed allyl ethers of starch, particularly those with an allyl content of 1.5 groups or more, are not stable substances and cannot be heated to remove the moisture without some polymerization and insolubilization. Therefore, for the determination of specific rotation the samples were dissolved in redistilled chloroform, dried overnight with anhydrous sodium sulfate, clarified with filter aid, and filtered through a mat of the same substance. The exact concentration was determined by pipetting 20 cc. of the solution into a tared dish and evaporating the solvent in a vacuum oven to constant weight.

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